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Alternative Alkalis in Peroxide Bleaching of Mechanical Pulp

ABSTRACT

Suitability of Magnesium Hydroxide, Magnesium Oxide, Calcium Hydroxide and Calcium Oxide as Sodium Hydroxide-replacing alkali in oxidizing hydrogen peroxide bleaching of mechanical pulp was studied. In the first stage, bleaching experiments of laboratory scale were carried out both using Sodium Silicate stabilizer and without it in medium consistency (10%). It was found that the most suitable alternative alkali is Magnesium Hydroxide, which needed no Sodium Silicate-stabilisation to achieve maximum brightness result of 77.0%-ISO whereas NaOH with Sodium Silicate gave 78.4%-ISO.

$Mg(OH)_2$ was then subjected to high-consistency (20%) laboratory bleaching experiments. According to the results replacing Sodium-based chemicals with $Mg(OH)_2$ produces about one percent (ISO) lower final brightness. To counter-balance this brightness loss $Mg(OH)_2$-alkali dissolves only some 45% of the organic carbon compounds compared to Sodium-based bleaching process. Similar results were obtained using technical grade $Mg(OH)_2$ in paper mill experiments. It was also found that it is possible, although not completely feasible to replace NaOH only partially with $Mg(OH)_2$. Where TOC in wastewaters of mechanical pulp peroxide bleaching stage pose a problem, one distinct and true possibility is to use $Mg(OH)_2$ as alkali.

INTRODUCTION

The most effective way of increasing brightness of mechanical pulp is known to be oxidizing hydrogen peroxide bleaching under strongly alkaline conditions. Traditionally these alkaline conditions have been created with Sodium Hydroxide and Sodium Silicate addition. However, using NaOH together with Sodium Silicate as bleaching auxiliary has undesired side-effects through dissolving great amounts of carbon-based compounds to bleaching filtrate. Ever more rigorous environmental licenses have urged on coming up with an effective but less carbon-dissolving replacement of NaOH as peroxide bleaching alkali. Also the possibility to withdraw from using Sodium Silicate as stabiliser is investigated. The aim of this study is to produce new and reliable information on the suitability and performance of alkali compounds that are alternative to Sodium-based chemicals.

Alternative alkalis have been studied before: for example *Pykäläinen et al.* concluded in 1993 that not only $Mg(OH)_2$ together with Sodium Silicate but also Magnesium Oxide and Calcium Hydroxide gave brightness results exceeding those of NaOH-Na_2SiO_3 combination while still producing lower COD_{Cr} loads [1]. Also in 2002 *Johnson et al.* were able to exceed the brightness values of conventional bleaching using $Mg(OH)_2$ while lowering COD of filtrate [2]. In 2005 *Li et al.* used $Mg(OH)_2$-alkali successfully at Irving Paper TMP mill bleaching sequence and were able to reduce bleaching costs, decreased COD of filtrates and finally decreased the amount of anionic trash [3].

MATERIALS AND METHODS

An unbleached and mill-chelated Norway Spruce pressure ground wood pulp sample was obtained from a Finnish paper mill from twin-wire press in consistency of 27.5%. Initial brightness of pulp sample was measured being 65.1%-ISO. In the preliminary stage a PGW pulp sample was subjected to peroxide bleaching in a plastic bag with 3.0% hydrogen peroxide dose in 10% consistency and 60°C temperature for 120 minutes with varying the alkali type and dose. Mixing was arranged manually.

In the second stage the conditions of experiments remained unchanged except for the consistency, which was set at 20%. This required bleaching chemicals to be mixed into pulp with a special Z-arm laboratory kneader. An option of partially replacing NaOH with $Mg(OH)_2$ was also experimented by using both alkalis in different ratios. All chemicals used were of *pro analysis* or equivalent grade. Experimental set-up used is presented in Figure 1.

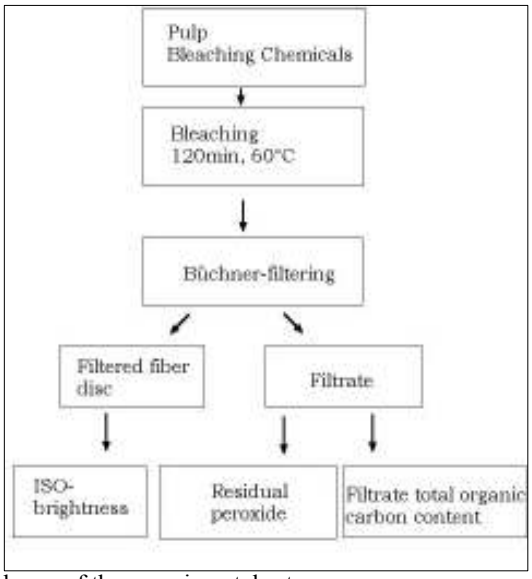

Figure 1. Guideline-scheme of the experimental set-up

An amount of bleached pulp representing about 7g of dry matter was filtered using a Büchner-funnel and the pulp disc was wet-pressed and drum-dried. Final brightness of the pulp was measured from the surface of dry pulp discs using Elrepho 2000-spectrophotometer. The amount of residual peroxide in bleaching filtrate was measured using a standard titration method KCL 214:85 and the total organic carbon content with a Shimadzu TOC 5050A-analyzer.

RESULTS AND DISCUSSION

Using Sodium Hydroxide and Sodium Silicate as peroxide bleaching alkalis yielded the highest baseline brightness value of 78.4%-ISO on chemical doses of respectively 2.1% and 1.0%. All doses are calculated relative to the weight of dry pulp. The total organic carbon content of bleaching filtrate was 1874 ppm. This result was considered as a reference point against which all of the alternative alkalis were compared to. Brightness values gained using 1.0% dose of each alternative alkali are presented in Figure 2.

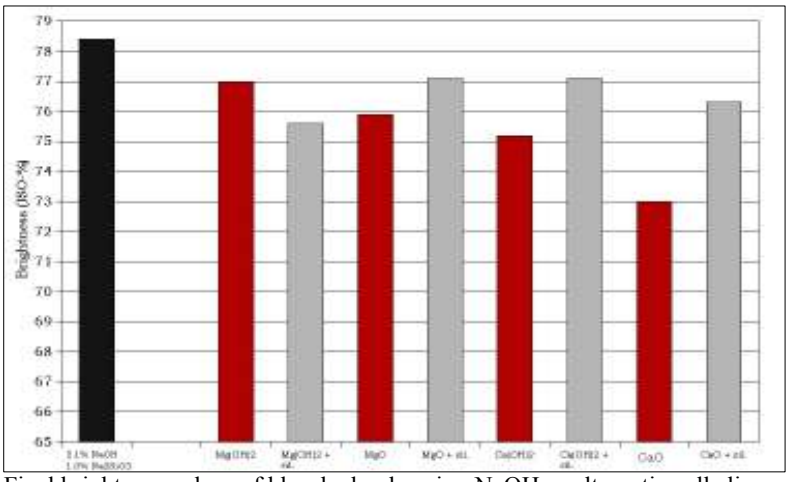

Figure 2. Final brightness values of bleached pulp using NaOH or alternative alkalis. Bleaching conditions: alkali dose 2.1% for NaOH, otherwise 1.0%, silicate dose 1.0% where used, hydrogen peroxide dose 3.0%, consistency 10%, time 120min and temperature 60°C.

As seen in Figure 2 the combination of NaOH and Na_2SiO_3 produces the best bleaching result in terms of brightness. Magnesium Oxide and Calcium Hydroxide reach a brightness level of 77%-ISO when 1.0% dose of

Sodium Silicate was also added. However, the use of $Mg(OH)_2$ gives final brightness of 77.0%-ISO with no Na_2SiO_3 addition. The amount of organic carbon in bleaching filtrate was measured and these results are presented as Figure 3.

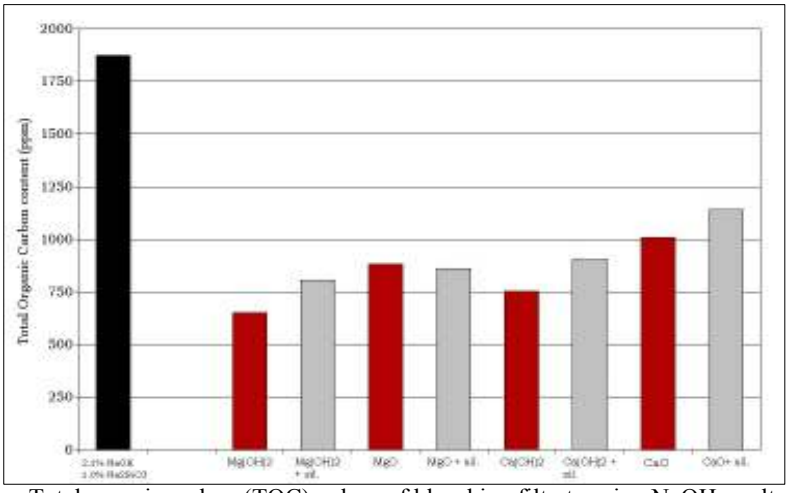

Figure 3. Total organic carbon (TOC) values of bleaching filtrate using NaOH or alternative alkalis. Bleaching conditions: alkali dose 2.1% for NaOH, otherwise 1.0%, silicate dose 1.0% where used, hydrogen peroxide dose 3.0%, consistency 10%, time 120min and temperature 60°C.

Figure 3 states that the best alkali in terms of low carbon dissolving in peroxide bleaching is Magnesium Hydroxide, TOC value being Sodium Silicate addition to peroxide bleaching 650 ppm. Of the alkalis tested in this experiment both MgO and $Ca(OH)_2$ suffer from their need of Sodium Silicate stabilization in order to achieve acceptable final brightness. Using Sodium Silicate together with $Mg(OH)_2$ seemed to have only negative effect on bleaching result. $Mg(OH)_2$ was chosen for further experiments in high consistency.

High-consistency bleaching experiments were carried out using an optimal combination of NaOH and Na_2SiO_3 in order to establish baseline brightness and TOC results. Then three different doses of $Mg(OH)_2$ were used and these results were made into Figure 4.

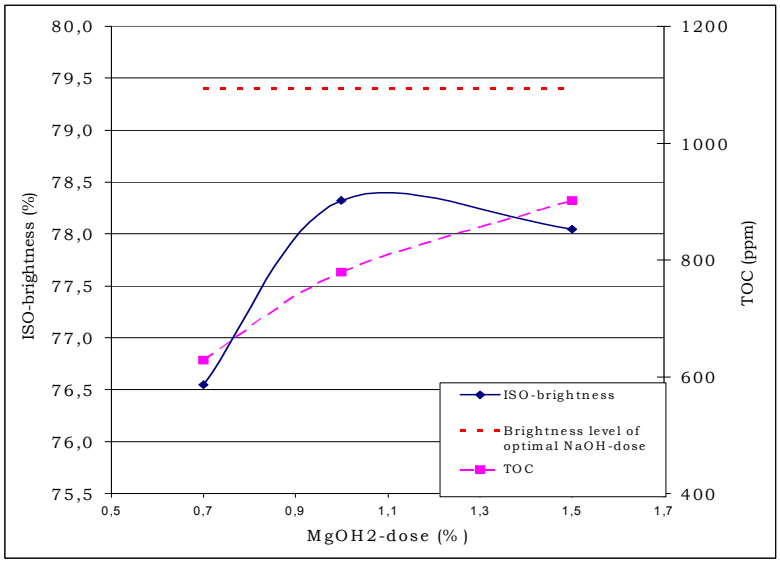

Figure 4. The effect of $Mg(OH)_2$-dose on final brightness of bleached PGW pulp and TOC of bleaching filtrate compared to 2.1% NaOH and 1.0% Na_2SiO_3. Bleaching conditions: hydrogen peroxide dose 3.0%, consistency 20%, time 120min and temperature 60°C.

As it can be seen from Figure 4, no amount of $Mg(OH)_2$ will produce a brightness value similar or exceeding to those of 2.1% NaOH and 1.0% Na_2SiO_3 (79.4%-ISO). The best result was achieved using $Mg(OH)_2$-dose of 1.0%. When NaOH and Sodium Silicate were used the TOC of bleaching filtrate was high, little over 1700ppm.

Optimal dose of $Mg(OH)_2$ gave brightness result of 78.3%-ISO, just one percent lower than using conventional chemicals. In return 1.0% dose of $Mg(OH)_2$ left organic compounds mostly intact and so TOC of filtrate was only 780ppm. In other words, replacing NaOH and Na_2SiO_3 with $Mg(OH)_2$ alone lowered TOC by almost 1000ppm, more than one half. It was also found that using $Mg(OH)_2$ conserved large portion of hydrogen peroxide added. Residual peroxide measurements showed that only 45% of 3.0% added H_2O_2 had reacted. These results were further confirmed by bleaching experiments conducted at a Finnish paper mill in laboratory scale using water and pulp samples taken directly from process. Similarity with mill conditions was ensured by using Magnesium Hydroxide of technical, commercially available grade. Results were in accordance with laboratory experiments conducted with *pro analysis*-grade chemicals and simplified conditions.

The possibility of partially replacing Sodium-based bleaching auxiliaries was studied by conducting high-consistency bleaching experiments as described above both with and without Sodium Silicate addition. Amounts of NaOH and $Mg(OH)_2$ were calculated respective to their determined optimum doses but Sodium Silicate dose when used was kept constant 1.0% for simplicity. Brightness and TOC results of partially-replacing NaOH experiments without Sodium Silicate addition are presented in Figure 5.

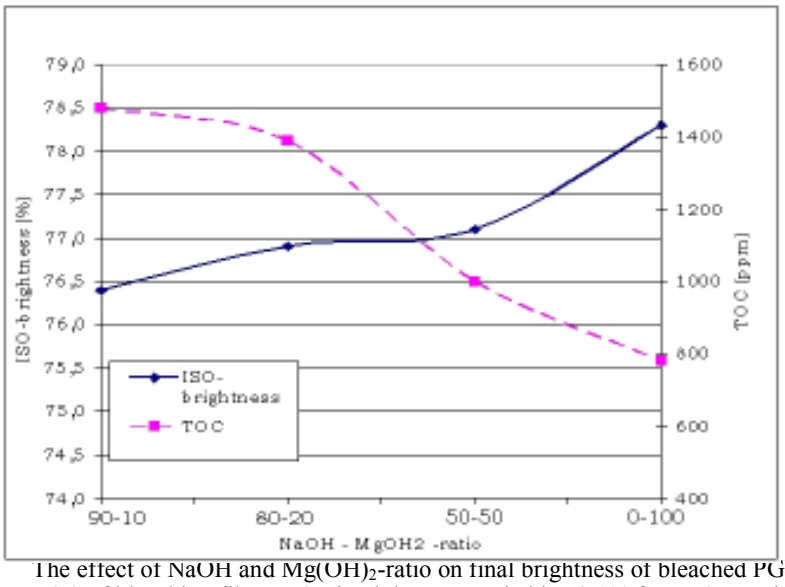

Figure 5. The effect of NaOH and $Mg(OH)_2$-ratio on final brightness of bleached PGW pulp and TOC of bleaching filtrate. Optimal doses were held at 2.1% for NaOH and 1.0% for $Mg(OH)_2$. Bleaching conditions: hydrogen peroxide dose 3.0%, consistency 20%, time 120min and temperature 60°C.

Figure 5 states that without Sodium Silicate stabilizing there is very poor bleaching performance with high NaOH ratios. Also the TOC load of wastewater is high, about 1500ppm. Higher portions of $Mg(OH)_2$ do help a little, but the most attractive results are achieved with full 100% $Mg(OH)_2$-dose and no NaOH at all. Applying default 1.0% Sodium Silicate dose turns the table, which is given as Figure 6.

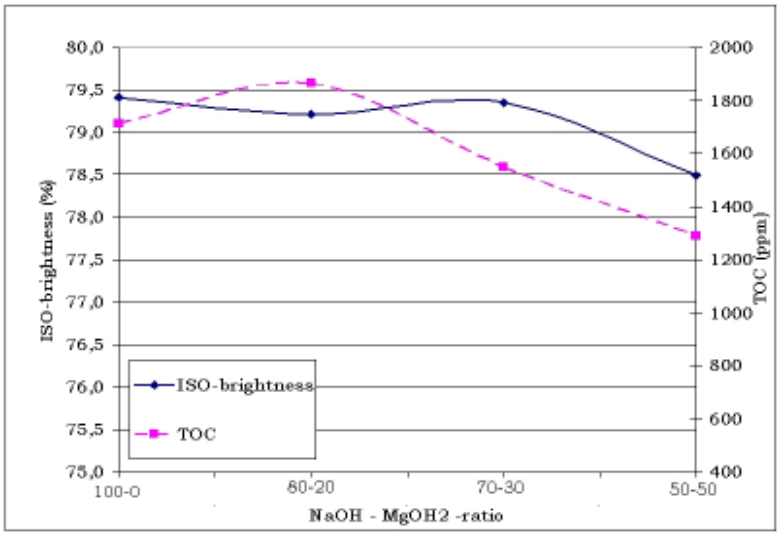

Figure 6. The effect of NaOH and $Mg(OH)_2$-ratio on final brightness of bleached PGW pulp and TOC of bleaching filtrate. Optimal doses were held at 2.1% for NaOH and 1.0% for $Mg(OH)_2$. Bleaching conditions: hydrogen peroxide dose 3.0%, silicate dose 1.0% consistency 20%, time 120min and temperature 60°C.

Comparing to Figure 5 adding Sodium Silicate expectedly enhances the performance of NaOH in terms of brightness gain. There is no significant change in either brightness or TOC values until mixture ratio of 50:50. Then the brightness result is deteriorated as found in medium consistency experiments. Using $Mg(OH)_2$ instead of NaOH obviously lowers the TOC value of bleaching filtrate. Should Sodium Silicate be used in bleaching sequence there is no real point in partially replacing NaOH with $Mg(OH)_2$.

CONCLUSIONS

Replacing Sodium Hydroxide and Sodium Silicate with alternative alkalis is a true option. The most prominent alternative to Sodium-based bleaching auxiliaries was found to be Magnesium Hydroxide. Bleaching with $Mg(OH)_2$-alkali needed no external stabilization in order to reach maximum final brightness. While $Mg(OH)_2$ gave about one ISO-percent brightness loss compared to conventional combination Na-chemicals it lowered TOC of bleaching filtrate by more than a half. Where the dissolved carbon content of peroxide bleaching wastewaters pose a significant problem, the change of alkali to Magnesium Hydroxide may well prove to be an efficient solution.

ACKNOWLEDGEMENTS

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APPENDIX

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2. Johnson D, Park S, Genco J, Gibson A, Wajer M, Branch B, Hydrogen Peroxide Bleaching of TMP Pulps Using $Mg(OH)_2$,TAPPI Fall Conference, San Diego, September 8-11, 2002.

3. Li Z, Court R, Belliveau M, Crowell M, Murphy R, Gibson A, Wajer M, Branch B, Ni Y, Using magnesium hydroxide as the alkali source in peroxide bleaching at Irving paper, Pulp & Paper Canada 106(2005) 6, p. 24-27.